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Proton Affinities of Nitrogen Oxyradicals

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• proton affinity (G2) calculations

The proton affinities (PA's) of nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3) as well as those of the *cis*- and *trans*-hydrogenhyponitrite (HONNO) and *cis*- and *trans*-dioxodinitrate ($ONNO^-$) radicals were calculated by semi-empirical quantum mechanical calculations (standard Gaussian-2 procedure). The PA calculated values of NO (518.8 kJ mol^{-1}), NO_2 (580.5 kJ mol^{-1}) and HNO_3 (746.0 kJ mol^{-1}) agree with the experimental values. The PA values for the NO_3, $ONNO^-$ and HONNO radicals were calculated and adjusted to 580, 1330 and 770 kJ mol^{-1}, respectively.

INTRODUCTION

During our investigations of the protonation/proton affinity of nitrogen oxides and their conjugate acids[1–4] it became evident (i) that this property can be calculated reliably by advanced quantum chemical methods, and (ii) that it is also important to determine this parameter for certain critical N–O radicals. The properties of radicals usually pose problems for quantum chemical calculations, and this is compounded by the fact that experimental values are scarce and direct tests of the computations are impossible. However, the proton affinities of the typical representatives $NO^\bullet$ and $NO_2^\bullet$ are known.[5] The photochemistry and reactions of $NO^\bullet$ and $NO_2^\bullet$ with other oxy and peroxy radicals in the atmosphere are of paramount importance for tropospheric ozone production and air pollution.[6–9] We are particularly interested in the proton affinities of the radicals $NO_3^\bullet$, $ONNO^{\bullet-}$ and $HONNO^\bullet$, which are also of importance in atmospheric and combustion chemistry. Thus, $NO_3^\bullet$, which is formed from $NO_2^\bullet$ and ozone, represents the major nighttime oxidant in the lower atmosphere.[10,11] The $ONNO^{\bullet-}$ is particularly interesting because calculations as well as photoelectron spectroscopy results[12] indicate that there are several forms of this species and that, surprisingly, the one with C_{2v} symmetry (*i.e.*, with both oxygen atoms at the same nitrogen) is the most stable. There are numerous high quality calculations of the electronic structure of the here mentioned nitrogen oxides,[13–19] but not of their proton affinities. In order to gain some insight into the behavior of the proton affinity values for anions, radicals and the acid forms of nitrogen oxides, we have calculated and compared them with the existing experimental data for three related series of such species. Encouraged by the good agreement between experiment and calculation for the radicals $NO^\bullet$ and $NO_2^\bullet$, we believe that the predicted proton affinities for the radicals $NO_3^\bullet$, $ONNO^{\bullet-}$ and $HONNO^\bullet$ are reliable and that they will prove useful until experimental values become available.

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CALCULATIONS

Standard Gaussian-2 (G2 procedure)[20–23] molecular energy calculations for 298 K were performed. The PA (α)'s, where α represents the sites of proton attack in the numbering system of atoms in Figure 1, were calculated. Figure 1 depicts the optimized structures of some of the most stable protonated forms. This particular PA (α) procedure, which yields G2 enthalpies for 298 K, was chosen because it provides the best correspondence with experiment. We evaluated the relative stability and the optimized structures of all isomers of the protonated substrate, a tactic that provided some insight into the energetics and the fates of the adducts (*i.e.*, possible fragmentation).

RESULTS AND DISCUSSIONS

The possibility of proton attachment to various positions, as indicated in the parentheses for individual compounds, yields different structures and PA values. The calculated PA's are given in Table I. We consider three series of compounds: anions, radicals and acids, which are mutually related by similar structures. For example, the $ONNO^-$ radical and HONNO radical are simultaneously the anion and acid radicals, respectively. Three experimental values,[5] the PA's for nitric acid (751.4 kJ mol^{-1}), nitric oxide (531.8 kJ mol^{-1}) and nitrogen dioxide (591.0 kJ mol^{-1}) compare well with the theoretically predicted values of 746.0, 518.8 and 580.5 kJ mol^{-1}, respectively. This agreement induces a considerable degree of confidence in the computed PA's of compounds for which experimental values are unavailable.

It is worth noting that a continuous decrease of PA is observed in the anion series whereas the radicals and acids exhibit a maximum at the middle, NO_2 and HNO_2, species. This may be because protonation of $NO^\bullet$ and HNO takes place preferably at the nitrogen atom; however, this is also the case of NO^-. It seems that charge neutralization is the most determinative factor for the PA's in the acid series. However, if one looks only at the protonation of the oxygen atoms in single nitrogen compounds, then PA is the highest for the middle species in all the three series.

The *cis*- and *trans*- forms of the radical $ONNO^{\bullet-}$ attach the proton both on nitrogen and oxygen with PA's in the range 1360–1380 kJ mol^{-1}, which is similar to the nitrate anion. Indeed, one might expect that all protonated forms will be generated under appropriate experimental conditions. However, an isomeric NNO_2^- radical structure also exists, as established by anion photoelectron spectroscopy[24] and matrix isolation experiments.[25] For this species, which was calculated to be of C_{2v} symmetry, and its photoelectron spectrum studied by Arnold and Neumark,[12] our PA calculations predict for the N1 nitrogen atom a slightly higher value than for the two O3 and O4 oxygen atoms, *i.e.*, 1350.6 and 1344.9 kJ mol^{-1}, respectively,

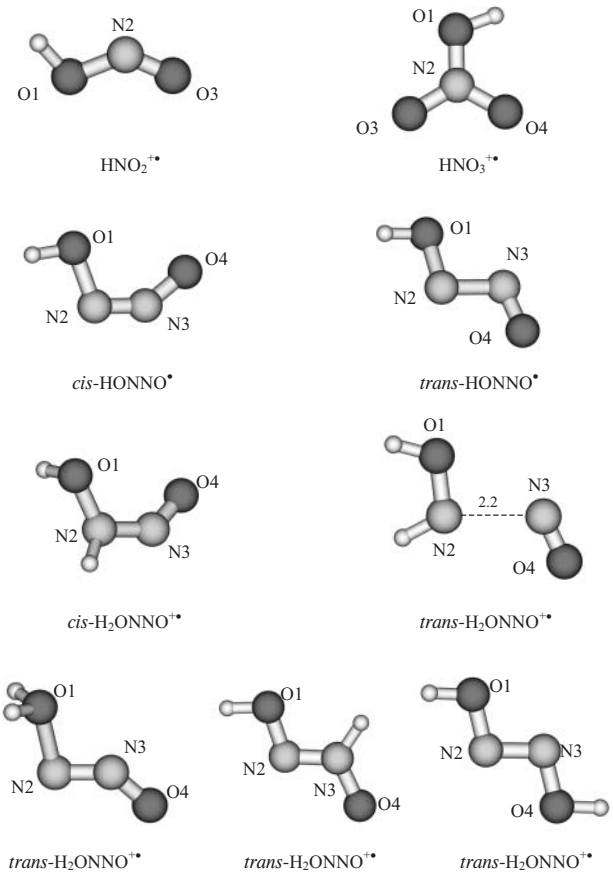

Figure 1. Structures of some of the more stable protonated forms of the compounds studied in this work. The positions of proton attack, α, for which calculations were performed are designated O1, O2, N3, *etc*.

and no protonation of N_2 (calculated PA is only 968.5 kJ mol^{-1}). Thus, these values are both lower than those found for the nitrogen and oxygen atoms protonation in the *cis*- and *trans*- forms of the isomeric $ONNO^{\bullet-}$. Because this species is just a reactive intermediate in the $O^- + N_2O$ reaction,[26] we did not evaluate the PA of the $HNNO_2$ species. Finally, the very important HONNO radical, according to the present calculations, is preferably protonated at the nitrogen atom (N2) adjacent to the OH group and, in its most stable *trans*-form, has a very high PA value of 760.4 kJ mol^{-1}. However, protonation of the *trans*-form at the other three positions: O4, N3 and O1 with PA's of 714.7, 707.1 and 695.0 kJ mol^{-1}, respectively, might also occur, particularly because N2-protonation leads to a structure with a very long N–N bond of 2.2 Å, a situation that does not occur for the other three protonated forms. Very similar PA values are obtained for the N2 and N3 protonation sites of the *cis*-form (691.6 *vs.* 679.8 kJ mol^{-1}, respectively) but, unfortunately, the calculations for O1 and O4 protonation did not converge.

In conclusion, comparison of the three available experimental values for NO, NO_2 and HNO_3 with their

TABLE I. Calculated and experimental proton affinities[a]

NO^-		$NO^\bullet$		HNO	
$\downarrow +H^+$		$\downarrow +H^+$		$\downarrow +H^+$	
HNO		$HNO^{\bullet+}$		H_2NO^+	
1516.0 (N)		518.8 (N)		693.3 (N)	
1339.3 (O)		457.5 (O)		622.0 (O)	
		Exp. 531.8			
NO_2^-		$NO^\bullet_2$		HNO_2	
$\downarrow +H^+$		$\downarrow +H^+$		$\downarrow +H^+$	
HNO_2		$HNO^\bullet_2{}^+$		$H_2NO_2^+$	
1413.8 (O)		580.5 (O)		780.3 (O1)	
1379.3 (N)		435.1 (N)		621.7 (N2)	
		Exp. 591.0		648.5 (O3)	
NO_3^-		$NO^\bullet_3$		HNO_3	
$\downarrow +H^+$		$\downarrow +H^+$		$\downarrow +H^+$	
HNO_3		$HNO^\bullet_3{}^+$		$H_2NO_3^+$	
1348.5		571.8 (O)		746.0 (O1)	
dissociative (N)		dissociative (N)		666.1 (O3)	
				625.5 (O4)	
				Exp. 751.4	
$^-ONNO^-$		$ONNO^{\bullet-}$		$HONNO^\bullet$	
$\downarrow +H^+$		$\downarrow +H^+$		$\downarrow +H^+$	
$HONNO^-$		$HONNO^\bullet$		$H_2ONNO^{\bullet+}$	
cis	*trans*	*cis*	*trans*	*cis*	*trans*
2065.2 (O1)	2002.5 (O1)	1375.6 (O)	1355.1 (O)	691.6 (N2)	695.0 (O1)
1982.6 (N2)	1974.2 (N2)	1364.4 (N)	1384.3 (N)	679.8 (N3)	760.4 (N2)
				not converge(O)	707.1 (N3)
					714.7 (O4)
		$NNO_2^{\bullet-}$			
		$\downarrow +H^+$			
		$HNNO_2^\bullet$			
		C_{2v}-symmetry			
		1350.6 (N1)			
		968.5 (N2)			
		1344.9 (O3, O4)			

[a] The positions of protonation, α, are depicted in Figure 1. All values are given in kJ mol^{-1}.

computed counterpart values indicate a slight underestimation of ~10 kJ mol^{-1} for the latter. Thus, the calculated proton affinities for the NO_3, $ONNO^-$ and HONNO radicals should be adjusted to 580, 1380 and 770 kJ mol^{-1}, respectively.

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SAŽETAK

Protonski afiniteti dušikovih oksiradikala

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Rabeći semi-empirijske kvantno mehaničke račune (standardna Gaussian-2 procedura) izračunani su protonski afiniteti (PA) za dušikov oksid, dušikov dioksid, nitratnu kiselinu, te za *cis*- i *trans*-hidrogenhiponitrit i *cis*- i *trans*-dioksidinitrat radikale. Izračunane PA vrijednosti za NO (518.8 kJ mol^{-1}), NO_2 (580.5 kJ mol^{-1}) i HNO_3 (746.0 kJ mol^{-1}) dobro se slažu s eksperimentalnim vrijednostima. Izračunana PA vrijednost za NO_3 radikal je 580 kJ mol^{-1}, za $ONNO^-$ radikal 1330 kJ mol^{-1}, a za HONNO radikal 770 kJ mol^{-1}.